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(54) Title: DENTAL PORCELAINS

(57) Abstract: Opaque porcelains for use with metal cores in the manufacture of PFM restorations. The porcelains exhibit a coefficient of thermal expansion (CTE) substantially equal to or slightly above the CTE of the metal to which it is applied. The porcelains exhibit a CTE equal to or up to about $1.5 \times 10^{-6}/^{\circ}\text{C}$ higher than the dental alloys to which they are applied as the opaque. The porcelains are fabricated from a mixture of two frit compositions. A high expansion, leucite containing frit is combined with a low melting glass frit to provide a porcelain having an expansion in the range of 16.9 to about $18 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25° - 500°C.

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DENTAL PORCELAINS

Field of the Invention

This invention relates to low fusing high-expansion dental porcelain especially useful for the fabrication of both all-ceramic and porcelain-fused-to-metal (PFM) restorations.

5 Background of the Invention

Porcelains are typically designed to be used in the manufacture of either all-ceramic dental restorations or in PFM restorations, but are not normally functional with both types of restorations due to the differences in properties of ceramics and metals. One such porcelain, OPC® Low Wear™ porcelain, available from
10 Jeneric/Pentron Inc., Wallingford, CT and covered in copending, commonly assigned patent application No. 09/133,582 filed August 13, 1998 which is hereby incorporated by reference, was initially designed to be used as overlay for pressed all-ceramic restorations as well as for the fabrication of porcelain jacket crowns and veneers. However, OPC® Low Wear™ porcelain is not currently used for PFM restorations
15 despite its wear resistance, forgiveness to natural dentition and strength being superior to those of conventional PFM porcelains as shown in the Table 1 below:

Table 1

Property	OPC® Low Wear™ Porcelain	Conventional Porcelain for PFM
Leucite average grain Size, μm	About 2-3	About 5-8
Leucite volume fraction, %	35-40	20-25
Enamel wear*, $\times 10^{-2}\text{mm}^2$	7.69 \pm 3.20	18.23 \pm 5.20
Wear of ceramics*, $\times 10^{-2}\text{mm}^3$	0.16 \pm 0.04	0.49 \pm 0.11
CTE, $10^{-6}/^{\circ}\text{C}$, 25 $^{\circ}\text{C}$ -500 $^{\circ}\text{C}$	About 17	About 13

- The major obstacle preventing use of the OPC® Low Wear™ porcelain in PFM restorations is the absence of an opaque/alloy combination compatible with this porcelain having relatively high expansion of about $17 \times 10^{-6}/^{\circ}\text{C}$ (25 $^{\circ}\text{C}$ -500 $^{\circ}\text{C}$).

- There exists a Golden Gate System™ for PFM restorations available through Degussa™ (Dental Division, South Plainfield, NJ) which combines Duceragold™ porcelain and Degunorm™, type IV crown and bridge alloy (CTE= $16.4 \times 10^{-6}/^{\circ}\text{C}$, 25 $^{\circ}\text{C}$ -500 $^{\circ}\text{C}$). This system requires rather tedious multistep alloy preparation procedures including a necessary wash bake step prior to application of the opaque; and an excessively long (16-20 min) and complex first dentine bake to assure proper bonding and compatibility of the Duceragold™ porcelain to the Degunorm™ alloy. In particular, the cooling segment (3-4 min between 720 $^{\circ}\text{C}$ and 680 $^{\circ}\text{C}$) in the first dentine bake is required by the manufacturer to grow additional leucite and may be an indication of instability of leucite in this porcelain. The following Table 2 below sets forth the various properties of the Duceragold™ porcelain.

Table 2

	Duceragold™
Firing Temperature, $^{\circ}\text{C}$	770-790
Glass Transition Temperature, $^{\circ}\text{C}$	490
Softening Temperature, $^{\circ}\text{C}$	595
CTE 25 $^{\circ}$ -500 $^{\circ}\text{C}$, $10^{-6}/^{\circ}\text{C}$	15.8
Recommended alloy	Degunorm
Alloy CTE 25 $^{\circ}$ -500 $^{\circ}\text{C}$, $10^{-6}/^{\circ}\text{C}$	16.4

U.S. Patent No. 5,453,290 to Van der Zel is directed to a dental porcelain for use with a dental alloy. The porcelain described therein must be fabricated from three frits, making it more difficult and costly to control the expansion and the glass transition temperature of the final product. Moreover, the CTE of the porcelain must be below the CTE of the alloy by 0.5 – 1.5 limiting the components to be used together. There is a need to provide a porcelain-fused-to-metal system for dental restorations having simple manufacturing procedures. It is desirable to provide a porcelain that is compatible with alloys of relatively high expansion. It is desirable to provide a two-frit porcelain for use in PFM restorations.

Summary of the Invention

These and other objects and advantages are accomplished by opaque porcelains for use with metal cores in the manufacture of PFM restorations. The porcelains exhibit a coefficient of thermal expansion (CTE) substantially equal to or slightly above the CTE of the metal to which it is applied. In a preferred embodiment, the porcelains exhibit a CTE equal to or up to about $1.0 \times 10^{-6}/^{\circ}\text{C}$ higher than the dental alloys to which they are applied as the opaque. The porcelains are fabricated from a mixture of two frit compositions. A high expansion, leucite containing frit is combined with a low fusing glass frit to provide a porcelain having an expansion in the range of 16.9 to about $18.5 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of $25^{\circ} - 500^{\circ}\text{C}$. By combining two frits, the expansion and fusing temperature can be controlled to the values stated above.

Description of the Invention

The invention relates to a porcelain material for use in all-ceramic restorations and PFM restorations. The porcelains exhibit a coefficient of thermal expansion (CTE) substantially equal to or slightly above the CTE of the metal to which it is applied. Preferably, the porcelains exhibit a CTE equal to or up to about $1.5 \times 10^{-6}/^{\circ}\text{C}$ higher than the dental alloys to which they are applied as the opaque, and more

preferably equal to or up to about $1.0 \times 10^{-6}/^{\circ}\text{C}$. The porcelains are compatible with metals having coefficients of thermal expansion (CTE) in the range of from about 15.5 to about $17 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range from 20° to 500°C . The porcelains exhibit CTEs in the range of about 16.9 to about 18.5 in the temperature range from 20° to 500°C , and preferably in the range of about 17 to about $17.5 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range from 20° to 500°C . The porcelains are fabricated from a mixture of two frit compositions. A high expansion, leucite containing frit is combined with a low fusing glass frit to provide a porcelain having an expansion in the range of 16.9 to about $18.5 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25° - 500°C . It is essential to this invention that both the high expansion and the low fusing components of the two-frit mixture exhibit a low glass transition temperature (GTT). It is extremely important that the low fusing component used in the opaque formulation exhibits a GTT lower than about 415°C . By combining two frits, the expansion and firing temperature can be controlled to the values stated above. Opaque porcelains herein having pigments exhibit a coefficient of thermal expansion of average value of about $17 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25° - 500°C . Opaque porcelains without pigments, i.e., white opaques, exhibit coefficients of thermal expansion in the higher end of the range, such as about 17.5 to about $18.5 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25° - 500°C .

Table 3 below shows the compositional ranges of the porcelains for use in the invention.

Table 3

	Body and Incisal Porcelain	Opaque Porcelain
SiO ₂	59-65	59-65
B ₂ O ₃	X	X
Al ₂ O ₃	10-15	10-15
ZnO	X	X
CaO	0.5-2	0.5-2
MgO	X	X
BaO	X	X
Li ₂ O	1.5-3	1.5-3
K ₂ O	15-17	15-17
Na ₂ O	4-6	4-6
TiO ₂	X	X
ZrO ₂	X	X
CeO ₂	X	X
F	0.4-1	0.4-1
Ta ₂ O ₅	----	X
SnO ₂	----	----
*Opacifiers	0-1	13-20
**Pigments	0-5	2-13

5 *Opacifiers, TiO₂, ZrO₂, ZrSiO₄, ZnO, CeO₂, or Ta₂O₅, are admixed as fine powder to a mixture of two frits. The resulting composition is referred to below as White Porcelain (opaque, body or incisal)

**Pigments are admixed as fine powder to a White Porcelain powder. The resulting powder composition is referred to below as Shaded Porcelain (opaque, body or incisal)

10 X signifies non-essential components

As set forth in Table 3 above, Li₂O, present in an amount of from about 1.5% to about 3%, and F, present in an amount of 0.4%-1%, are instrumental in providing a low glass transition temperature. The presence of Li₂O and F also assist as well in increasing the coefficient of thermal expansion and decreasing the maturing (firing) temperature. The high expansion, leucite containing component of the two-frit mixture has a reasonably low glass transition temperature as well. This is achieved by maintaining a reasonably low molar ratio of Al₂O₃ to the sum of alkali and alkaline

- earth oxides (R₂O+RO). Normally, these compositions are extremely unstable and reactive as well as prone to sanidine precipitation in the temperature range of 650°C-950°C. It was surprisingly found that certain compositions with specific combinations of K₂O, Na₂O and Li₂O are very stable. In addition, it was found that the molar ratio of Al₂O₃/K₂O should be within the range of 0.73-0.95 to assure both the required thermal stability and low glass transition temperature of the high expansion component of the porcelain. The low glass transition temperature provides a porcelain having good compatability with alloys having CTEs in the range of about 15.5 to about 17 x 10⁻⁶/°C in the temperature range of 25 ° – 500 ° C. Table 4 below sets forth the properties of the porcelain compositions.

Table 4

PORCELAIN	Body & Incisal	Opaque
Firing Temperature, °C	855-870	855-890
Glass Transition Temperature, °C	420-430	430-440
Softening Temperature, °C	520	---
CTE 25° - 400°C, 10 ⁻⁶ /°C	15.2	---
CTE 25° - GTT, 10 ⁻⁶ /°C	15.8 (GTT=430 °C)	---
CTE 25° -500°C, 10 ⁻⁶ /°C	17.2	17.0

- Table 5 sets forth compatible alloys for use with the porcelains.

Table 5

Alloy	CTE (25°C-500°C)	Application
Bio-75G	15.5±0.2	Fast Cool for single units only
GoldCore 75	16.4±0.2	For single units and bridges
GoldCore 55	17.0±0.2	For single units and bridges
JewelCast	17.0±0.2	For single units and bridges

Table 6 below shows compositional examples of body (incisal) and opaque porcelains.

Table 6

	Example 1 Body/Incisal Porcelain	Comparative Example 1	Example 2 White Opaque Porcelain for Light* Shades	Example 3 White Opaque Porcelain for Light* Shades	Example 4 White Opaque Porcelain for Dark** Shades	Example 5 White Opaque Porcelain for Dark** Shades
Two-frit Mixture Composition:						
SiO ₂	61.9	61.5	60.0	58.5	60.1	58.6
B ₂ O ₃	0.5	0.5	0.6	0.6	0.6	0.6
Al ₂ O ₃	11.6	15.4	13.6	13.6	13.7	13.6
ZnO	0.0	0.0	0.0	2.0	0.0	2.0
CaO	1.7	0.6	1.2	1.2	1.2	1.2
MgO	0.8	0.2	0.2	0.1	0.2	0.1
BaO	0.0	0.0	0.4	0.4	0.4	0.4
Li ₂ O	2.5	2.3	2.3	2.3	2.3	2.3
K ₂ O	15.7	12.9	15.1	15.0	15.1	15.0
Ta ₂ O ₅	0.0		0.0	0.0	0.0	0.0
Na ₂ O	4.8	5.0	5.5	5.4	5.4	5.3
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0
ZrO ₂	0.0	0.0	0.0	0.0	0.0	0.0
CeO ₂	0.0	0.6	0.3	0.3	0.3	0.3
F	0.6		0.7	0.6	0.7	0.6
Mixed-in Opacifiers:						
ZrO ₂			17	17	15	15
ZrSiO ₄						
TiO ₂						
SnO ₂						
ZnO						
CeO ₂						
Ta ₂ O ₅						
Firing temperature	857		871	871	871	871
CTE (25°C-500°C)	17.2±0.3		17.8	17.8	17.8	17.8

*Light Opaque Shades – Pigment content < 6wt%

**Dark Opaque Shades – Pigment content > 6wt%

The low glass transition temperature of the opaque porcelain is paramount to assure its compatibility with alloys having CTE's in the range of about 15.5 to about 17, such as commercially available Gold Core 75™ alloy from Jeneric/Pentron Inc., Wallingford, CT. This is a gold alloy that does not contain copper and other elements that form dark oxide layers and, therefore, requires much less intricate preparation procedures compared to the Degunorm alloy. Specifically, the Gold Core 75™ alloy forms an adequate oxide layer without compromising the appearance of the coping when degassed at 870 °C-885 °C for about 5-7 min in air or vacuum.

The high potassium content in the porcelain is essential to assure high stability of leucite. High potassium oxide content combined synergetically with other alkali elements (Li and Na) assures as well relatively low glass transition temperature (GTT) and, hence, increased resistance to thermal expansion mismatch cracking and increased adaptability to alloys of slightly lower expansion. It was surprisingly found that increased potassium content increases stability in compositions with low GTT, e.g., Example 1 was found to be much more stable than Comparative Example 1 (compare K₂O content). Specifically, dental porcelain of Example 1 has excellent thermal expansion stability and maintains the same thermal expansion after 5 successive bakes at its firing temperature. Dental porcelain of Comparative Example 1 was found to change thermal expansion and opacity upon multiple bakes.

Essential to this invention is that opaque compositions possess a relatively low transition temperature and contain the same elements such as ZnO and Ta₂O₅ as the oxide layer forming on the alloy that assure good bonding to alloys. Specifically, the oxide layer on the Gold Core 75™ alloy was found to be enriched with ZnO and Ta₂O₅ and the same components were included in the opaque formulation to improve bonding.

Body and incisal porcelain are typically applied to opaque porcelain, respectively. Preferably, the body and incisal porcelains used with the opaque herein exhibit an average coefficient of thermal expansion of about 17.2.

In a preferred embodiment of the invention, alloys having a CTE in the range of about 15.5 to about $17 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25 ° – 500 ° C are used

to manufacture a metal core for a restoration. Opaque porcelains are applied thereto, wherein the CTE is in the range of about 16.9 to about $17.5 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of $25^{\circ} - 500^{\circ}\text{C}$ and body porcelains are applied thereto having CTEs in the range of about 16.9 to about 17.7. It is preferable that the CTE of the
5 opaque is between the CTE of the alloy and the CTE of the body porcelain.

The following examples illustrate the invention.

Examples

Copings and bridge frameworks cast from Bio-75G, GoldCore75, GoldCore55
10 and JewelCast alloys available from Jeneric/Pentron, Wallingford, CT, were prepared with a carbide tool, sand-blasted with alumina sand at pressure of 2 bar and ultrasonically cleaned in water for about 5 min. The same degassing cycle given in the firing charts below was used for Bio-75G, JewelCast, GoldCore55 and GoldCore75
15 castings. Following degassing, the oxide layer was removed by sand-blasting and castings were ultrasonically cleaned in water for about 5 min. The opaque of the composition of Example 3 (Table 6) was applied in two thin coats and fired according to the firing cycle given in a table below. Body/Incisal porcelain of composition of Example 1 was used to build full contour crowns and bridges and fired up to 5 times
as per firing chart below.

20 No cracking was observed on single unit restorations made from the alloys above. However, cracks in pontic areas were found when porcelain was fired onto bridge frameworks made from Bio-75G. Both single and multiunit restorations made from GoldCore 75, GoldCore 55 and JewelCast exhibited no cracking upon multiple firings.

Firing chart in °F

	Degassing cycle	Opaque bake (2 coats)	1 st OPC Low Wear bake	2 nd OPC Low Wear bake	3 rd -5 th OPC Low Wear bake
Predry, min	0	6	6	6	6
Low T, °F	1200	600	1000	1000	1000
High T, °F	1625	1600	1575	1550	1550
Rate, °C/min	100	75	75	75	75
Vacuum	100%	100%	100%	100%	100%
VacOn, °F	1200	750	1000	1000	1000
VacOff, °F	1625	1500	1525	1500	1500
Hold, min	5 in vacuum	0	0	0	0
Cool, min	0	0	0	0	0

Firing chart in °C

	Degassing cycle	Opaque bake (2 coats)	1 st OPC Low Wear bake	2 nd OPC Low Wear bake	3 rd -5 th OPC Low Wear bake
Predry, min	0	6	6	6	6
Low T, °C	650	316	538	538	538
High T, °C	885	871	857	843	843
Rate, °C/min	55	42	42	42	42
Vacuum	100%	100%	100%	100%	100%
VacOn, °C	650	399	538	538	538
VacOff, °C	885	816	829	816	816
Hold, min	5 in vacuum	0	0	0	0
Cool, min	0	0	0	0	0

- 5 In addition to dental restorations, bond flags were cast from the alloys listed above. Two thin coats of opaque (composition of Example 3) were applied and fired onto the bond flags. Bond flags were bent using pliers and metal surface exposed along the bend where opaque is fractured was inspected using optical stereomicroscope under magnification of 10x. Fracture along opaque-metal interface
- 10 was found mostly adhesive, i.e. substantial fraction of the metal surface was covered by opaque indicating good bonding between alloys and opaque. The observed coverage was comparable to other metal-porcelain systems and therefore deemed sufficient. Bond strength was quantified according to ISO-9693 Metal-Ceramic Bond

Test (Schwickerath crack initiation test). The following Table indicates the bond strengths calculated from the formula $\tau_b = k \cdot F_{fail}$

wherein τ_b is the debonding/crack initiation strength

k is a coefficient which is a function of the thickness of the

metal substrate, and the value of Young's modulus of the used metallic material; and

F_{fail} is the fracture force

Specimen	Thick- ness (mm)	Elastic Modulus (GPa)	Load (Lbs)	F(fail) Newtons	K	τ_b (MPa)
gold core 75	0.55	12.5	2.81	12.49950291	3.6	44.99821048
gold core 75	0.54	12.5	2.262	10.06187743	3.75	37.73204037
gold core 75	0.55	12.5	1.81	8.051281235	3.65	29.38717651
gold core 75	0.55	12.5	3.02	13.43362946	3.65	49.03274754
gold core 75	0.55	12.5	2.78	12.36605626	3.65	45.13610535
mean				0		41.25725605
Std Dev				0		7.791412161
gold core 55	0.5	15.12	1.42	6.316474781	4.1	25.8975466
gold core 55	0.5	15.12	1.07	4.759597194	4.1	19.5143485
gold core 55	0.52	15.12	2.88	12.81087843	3.8	48.68133803
gold core 55	0.5	15.12	1.68	7.473012417	4.1	30.63935091
gold core 55	0.47	15.12	1.51	6.716814732	4.7	31.56902924
gold core 55	0.47	15.12	0.98	4.359257243	4.7	20.48850904
mean				0		29.46502039
Std dev						9.724481694

As will be appreciated, the present invention provides porcelain compositions compatible with alloys for use in the manufacture of PFM restorations. The porcelains exhibit a coefficient of thermal expansion (CTE) substantially equal to or slightly above the CTE of the metal to which it is applied. The porcelains are fabricated from a mixture of two frit compositions. A high expansion, leucite containing frit is combined with a low melting glass frit to provide a porcelain having

an expansion in the range of 16.9 to about $18 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25° - 500°C . By combining two frits, the expansion and firing temperature can be easily controlled.

While various descriptions of the present invention are described above, it
5 should be understood that the various features can be used singly or in any combination thereof. Therefore, this invention is not to be limited to only the specifically preferred embodiments depicted herein.

Further, it should be understood that variations and modifications within the spirit and scope of the invention may occur to those skilled in the art to which the
10 invention pertains. Accordingly, all expedient modifications readily attainable by one versed in the art from the disclosure set forth herein that are within the scope and spirit of the present invention are to be included as further embodiments of the present invention. The scope of the present invention is accordingly defined as set forth in the appended claims.

What Is Claimed Is:

1. A porcelain composition for use as an opaque on dental alloys in the manufacture of a dental restoration comprising by weight percent:

about 48 to about 65 % SiO_2 ;
about 10 to about 15 % Al_2O_3 ;
about 0.5 to about 2 % CaO ;
about 1.5 to about 3 % Li_2O ;
about 15 to about 17 % K_2O ;
about 4 to about 6 % Na_2O ; and
about 0.4 to about 1 F.

2. The porcelain of claim 1 possessing a coefficient of thermal expansion slightly higher than the dental alloys to which it is applied as the opaque.

3. The porcelain of claim 1 wherein the coefficient of thermal expansion is equal to or up to about $1.5 \times 10^{-6}/^\circ\text{C}$ higher than the dental alloys to which it is applied as the opaque.

4. The porcelain composition of claim 1 possessing a coefficient of thermal expansion which is compatible with alloys possessing a coefficient of thermal expansion in the range of about 15.5 to about $17 \times 10^{-6}/^\circ\text{C}$ in the temperature range of $25^\circ - 500^\circ\text{C}$.

5. The porcelain of claim 1 possessing a coefficient of thermal expansion of about 16.9 to about 18.5 in the temperature range of 25°C to 500°C .

6. The composition of claim 1 further comprising by weight:

about 0 to about 0.7 % B_2O_3 ;

about 0 to about 5 % ZnO ;

about 0 to about 2 % MgO ;

5 about 0 to about 1 % BaO ;

about 0 to about 2 % TiO_2 ;

about 0 to about 17 % ZrO_2 ;

about 0 to about 7 % $ZrSiO_4$;

about 0 to about 1 % CeO_2 ;

10 about 0 to about 2 % Ta_2O_5 ; and

about 0 to about 18 % SnO_2 .

7. A method of making a dental restoration comprising:

forming a dental porcelain powder from a dental composition

comprising

5 about 48 to about 65 % SiO_2 , about 10 to about 15 % Al_2O_3 , about 0.5 to about 2 %
CaO, about 1.5 to about 3 % Li_2O , about 14 to about 17 % K_2O , about 4 to about 6 %
Na₂O, and about 0.4 to about 1 F, wherein the maturing temperature is in the range of
about 750°C to about 890°C;

shaping the dental porcelain powder onto a metal core; and

heating the shaped dental porcelain powder to between about 750°C to

10 about

880°C to fuse the dental porcelain powder to the metal core;

wherein the metal core exhibits a coefficient of thermal

expansion in the range from about 15.5 to about $17 \times 10^{-6}/^{\circ}C$ (measured from 25°C to
500°C).

8. The method of claim 7 wherein the porcelain has a coefficient of thermal
in the range of about 17 to about 17.5 in the temperature range of 25°C to 470 °C

9. The method of claim 7 wherein the metal framework comprises a gold alloy.
10. The method of claim 7 wherein the porcelain powder is an opaque porcelain.
11. The method of claim 10 further comprising applying a body porcelain over the opaque porcelain.
12. The method of claim 11 further comprising applying an incisal porcelain over the body porcelain.
13. The method of claim 12 wherein the incisal porcelain comprises:
- about 59 to about 65 % SiO_2 ;
 - about 10 to about 15 % Al_2O_3 ;
 - about 0.5 to about 2 % CaO ;
 - about 1.5 to about 3 % Li_2O ;
 - about 15 to about 17 % K_2O ;
 - about 4 to about 6 % Na_2O ; and
 - about 0.4 to about 1 F.

14. A porcelain composition comprising by weight percent:

about 59 to about 65 % SiO_2 ;

about 10 to about 15 % Al_2O_3 ;

about 0.5 to about 2 % CaO ;

about 1.5 to about 3 % Li_2O ;

about 12 to about 17 % K_2O ;

about 4 to about 6 % Na_2O ;

about 0.4 to about 1 % F; and

about 10 to about 20 % of an opacifier;

wherein the porcelain composition is used as an opaque in the
manufacture of dental restorations.

15. The porcelain composition of claim 16 wherein the opacifier is
selected

from Al_2O_3 , ZnO , TiO_2 , ZrO_2 , ZrSiO_4 , CeO_2 , Ta_2O_5 , SnO_2 and mixtures thereof.

16. A dental restoration comprising:

a metal core, having a coefficient of thermal expansion below about $17 \times 10^{-6}/^\circ\text{C}$ (measured from 25°C to 500°C); and

an opaque porcelain applied on the metal core, having a coefficient of
thermal expansion about equal to or up to about $1.5 \times 10^{-6}/^\circ\text{C}$ higher than the metal
core.

17. The dental restoration of claim 16 wherein the opaque porcelain comprises by weight:

5 about 48 to about 65 % SiO_2 ;
 about 10 to about 15 % Al_2O_3 ;
 about 0.5 to about 2 % CaO ;
 about 1.5 to about 3 % Li_2O ;
 about 14 to about 17 % K_2O ;
 about 4 to about 6 % Na_2O ; and
 about 0.4 to about 1 F.

18. The dental restoration of claim 17 wherein the opaque porcelain further comprises:

5 about 0 to about 0.7 % B_2O_3 ;
 about 0 to about 5 % ZnO ;
 about 0 to about 2 % MgO ;
 about 0 to about 1 % BaO ;
 about 0 to about 2 % TiO_2 ;
 about 0 to about 17 % ZrO_2 ;
10 about 0 to about 7 % ZrSiO_4 ;
 about 0 to about 1 % CeO_2 ;
 about 0 to about 2 % Ta_2O_5 ; and
 about 0 to about 18 % SnO_2 .

19. A dental restoration comprising:

a metal core, having a coefficient of thermal expansion below about $17 \times 10^{-6}/^{\circ}\text{C}$ (measured from 25°C to 500°C);

5 an opaque porcelain applied on the metal core, having a coefficient of thermal expansion about equal to or up to about $1.5 \times 10^{-6}/^{\circ}\text{C}$ higher than the metal core; and

a body porcelain applied to the opaque porcelain having a coefficient
of
thermal expansion about equal to or up to about $1.5 \times 10^{-6}/^{\circ}\text{C}$ higher than the metal
10 core.

20. The dental restoration of claim 19 wherein the coefficient of thermal expansion of the opaque porcelain is between the coefficient of thermal expansion of the alloy and the coefficient of thermal expansion of the body porcelain.

INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/US 00/40296

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K6/02 C03C10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 653 791 A (DIMEGLIO LISA M ET AL) 5 August 1997 (1997-08-05) column 2, line 9 - column 3, line 51 column 5, line 20 - line 56 claims; tables	1,4-8, 10-13
X	EP 0 518 454 A (IVOCLAR AG) 16 December 1992 (1992-12-16) page 2, line 49 - page 3, line 2 page 3, line 17 - line 23 page 3, line 49 - line 51	1
X	EP 0 870 479 A (MEGADENTA GMBH DENTALPRODUKTE) 14 October 1998 (1998-10-14) column 4, line 10 - line 20	1
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

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PCT/US 00/40296

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 18910 A (JENERIC PENTRON INC ;PANZERA CARLINO (US)) 22 April 1999 (1999-04-22) page 5, line 11 -page 7, line 3 page 11, line 1 - line 10	1-13
A	WO 95 11866 A (MINNESOTA MINING & MFG) 4 May 1995 (1995-05-04)	
A	US 5 453 290 A (VAN DER ZEL JOSEPH M) 26 September 1995 (1995-09-26) cited in the application	
A	EP 0 272 745 A (AMERICAN THERMOCRAFT CORP) 29 June 1988 (1988-06-29)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inten. nat Application No

PCT/US 00/40296

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5653791 A	05-08-1997	AU 1621397 A CA 2199569 A EP 0795311 A JP 10036137 A US 5944884 A	22-01-1998 12-09-1997 17-09-1997 10-02-1998 31-08-1999
EP 0518454 A	16-12-1992	DE 4119483 A AT 126049 T AU 650338 B AU 1739592 A CA 2070691 A DE 59203186 D	24-12-1992 15-08-1995 16-06-1994 17-12-1992 14-12-1992 14-09-1995
EP 0870479 A	14-10-1998	DE 19714178 A	08-10-1998
WO 9918910 A	22-04-1999	AU 9802698 A	03-05-1999
WO 9511866 A	04-05-1995	US 5622551 A	22-04-1997
US 5453290 A	26-09-1995	NL 9001986 A AT 110254 T DE 475528 T DK 475528 T EP 0475528 A ES 2059042 T JP 4230611 A	01-04-1992 15-09-1994 25-02-1993 19-09-1994 18-03-1992 01-11-1994 19-08-1992
EP 0272745 A	29-06-1988	US 4798536 A AT 75137 T CA 1272222 A DE 3778513 A JP 63287709 A JP 1882859 C JP 6000662 B JP 63265856 A	17-01-1989 15-05-1992 31-07-1990 27-05-1992 24-11-1988 10-11-1994 05-01-1994 02-11-1988